# Determination of $^{99}$Tc in sea water and urine samples using TK-TcScint Resin-V 1.0-19/11/2024-TKI-TC01

## 1. Scope

This method aims to quantify $^{99}$Tc in seawater and urine samples using TK-TcScint Resin for simultaneous separation and quantification by liquid scintillation counting (LSC). This approach allows for higher sample throughput (samples can be processed in parallel) and provides a more time-efficient solution, as the samples can be measured overnight.

## 2. Summary

The reported method is based on the publication by (Barrera et al., 2016). Technetium-99 is produced during the lifecycle of nuclear power plants and is therefore present in waste samples that require characterization. The anion $TcO_4^-$ is highly mobile, making the presence of $^{99}$Tc in waste samples a potential environmental concern. Given its trace concentration, extensive methods have traditionally been employed to separate it from major elements in samples before quantification.

The development of a plastic scintillator resin (TK-TcScint Resin) enables the simultaneous preconcentration, separation, and quantification of $^{99}$Tc using liquid scintillation counting (LSC). This method was applied to real spiked samples, such as seawater and urine, yielding low deviations in results, demonstrating its reliability and efficiency.

## 3. Significance of use

This method proposes a fast, reliable, and efficient approach for quantifying $^{99}$Tc in various samples, enabling effective monitoring of $^{99}$Tc activity originating as waste from nuclear power plants.

## 4. Interferences

Given the nature of the resin, some evaluated interferences included chloride, nitrite and sulphate as chemical interferences and $^{36}$Cl and $^{238}$U/$^{234}$U as radioactive interferences potentially present in real samples. The removal of $^{36}$Cl during sample loading onto the resin was achieved using 0.5 M HCl, while uranium isotopes were effectively eluted from the column with a mixture of 0.1 M $HNO_3$ and 0.1 M HF.

## 5. Apparatus

a. Hot plate and stirrer
b. Analytical balance -0.0001 g sensitivity



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c. Muffle oven
d. Sand bath
e. Quantulus LS spectrometer (PerkinElmer) with logarithmic amplification, a multichannel analyser (MCA) (4096 channels distributed in four segments of 1024), alpha/beta discrimination and background reduction by active guard
f. Vacuum box
g. Peristaltic pump

## 6. Reagents

### a. *Reagents*

Unless otherwise indicated, all references to water should be understood to mean double deionized distilled water. All reagents should be at least of analytical grade.

- Tk-TcScint Resin 6 mL column vial (TK-TcScint resin produced in Triskem, France)
- Concentrated HCl solution (37%)
- $HNO_3$ 69% from PanReac (Castellar del Valles, Spain)
- Concentrated HF solution (49%)
- Stock solution $^{99}Tc$
- Stock solution $^{36}Cl$
- Stock solution $^{238}U/^{234}U$
- OptiPhase SuperMix cocktail (PerkinElmer, Whatman, MA, USA)

### b. *Preparation of solutions*

- 0.1 M HCl: For 100 mL solution add around 50 mL deionized water at the bottom of the 100 mL flask and add slowly 0.83 mL concentrated HCl (37% HCl). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
- 0.1 M HF and 0.1 M $HNO_3$: For 100 mL solution add around 50 mL deionized water at the bottom of the 100 mL flask and add slowly 0.64 mL concentrated $HNO_3$ (69% $HNO_3$) and 0.36 mL concentrated HF (49% HCl). Then, add water to the volumetric flask until the total volume. Mix thoroughly.
- 0.5 M HCl: For 100 mL solution add around 50 mL deionized water at the bottom of the 100 mL flask and add slowly 4.17 mL concentrated HCl (37% HCl). Then, add water to the volumetric flask until the total volume. Mix thoroughly.


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### c. *Samples used*

- Seawater sample (spiked with $^{99}$Tc and $^{36}$Cl as interference with final activity of 4.2 Bq)
- Urine samples

## 7. Procedure

### a. *Sample preparation*

*Preparation of active samples prior to TK-TcScint separation*

Seawater samples

1. Prepare samples to a final concentration of 0.1 M HCl (in double deionised water)
2. Spike stock solutions of $^{99}$Tc and $^{36}$Cl to a final activity of 4.20 Bq of each radionuclide ($^{36}$Cl considered as an interference)
3. In case uranium interferences might be expected, the activity of $^{238}$U/$^{234}$U to be spiked is 0.67 Bq
4. Blank samples in 0.1 M HCl (same composition but no active solution spiked)

Urine samples

1. Take 100 mL of urine sample
2. Mix with 10 mL of 65% $HNO_3$
3. Evaporate to dryness
4. Dissolve the residue in 5 mL of 65% $HNO_3$
5. Evaporate again to dryness
6. Heat to 550°C in a muffle oven for 30 min
7. Dissolve the residue in 3 mL of 65% $HNO_3$
8. Add 100 mL of double deionised water and 5 mL of $H_2O_2$
9. Heat to 90°C for 1 h in a sand bath (*ensure oxidation of Tc*)

### b. *Radiochemical separation*

*Preparation of Tc-PSresin column vials (TK-TcScint Resin)*

Fill a modified 6 mL column vial (with caps on both the bottom and top) with 3 g of TK-TcScint resin and 1.26 mL of double-deionized water. Immerse the column vial in an ultrasonic bath for 15 minutes to ensure homogenization. The flow rate was set to 0.5 mL/min for the complete separation procedure.

1. Connect the pump to the column vial for removing the remaining water on the vial
2. Conditioning: 5 mL 0.1 M HCl


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3. Loading: from the ~110 mL, take 10 mL and pass them through the TK-TcScint Resin

Seawater samples

4. Rinsing: 4 times 5 mL double deionized water
5. After last rinse step, pump for 60 min to ensure complete absence of solution on the vial/resin

Urine samples

4. 1st rinsing: 3 times 5 mL of a mixture of 0.1 M HF and 0.1 M $HNO_3$
5. 2nd rinsing: 1 time 5 mL double deionized water

$^{36}$Cl interference

4. 1st rinsing: 4 times 5 mL double deionized water
5. 2nd rinsing: 1 time 5 mL 0.5 M HCl

### c. *Sample measurement*

1. Disconnect TK-TcScint Resin column vial from the pump
2. Close the column vial with the two caps for measurement
3. Place the column vial on a 20 mL polyethylene scintillation vial and place the vial into the detector
4. Effluents (collected after loading and rinsing) were collected all together, and an aliquot of 6 mL is mixed with 14 mL of OptiPhase SuperMix cocktail for measurement. After that, the vial is placed on the detector
5. Prepare a protocol in the low coincidence bias and high-energy multichannel analyser configuration (detector: Quantulus detector)
6. Before the actual counting, vials are left on the dark for 2 h
7. Measurement of the samples is performed using 9 periods of 20 min with 3 seconds in each period for SQP(E) parameter
8. Rhenium is used as a tracer for chemical recovery evaluation; thus, Re is measured in the effluent fraction to ensure 100% retention on the PS Resin
    - Total efficiency includes both the detection efficiency of $^{99}$Tc and the chemical recovery for this radionuclide
    - Detection efficiency values are approximately 70% (70.0% ± 1.9%)



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## 8. References

Barrera, J., Tarancón, A., Bagán, H., & García, J. F. (2016). A new plastic scintillation resin for single-step separation, concentration and measurement of technetium-99. *Analytica Chimica Acta*, *936*, 259–266. https://doi.org/10.1016/j.aca.2016.07.008



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